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19. ABSTRACT (Continue on reverse if necessary and identify by block number)

Metal atom concentrations have been measured by atomic absorption to study plasma dry etching processes. The etch rate and the gas phase concentration of titanium metal atoms were observed as a function of total pressure during etching. A kinetic model and mechanism was developed which fit these data and suggested a second order dependence on fluorine atoms. Using atomic emission actinometry this dependence was confirmed, supporting the proposed model. The gas phase reaction rate of Ti with SF_5 was estimated to be fast, in the order of 10 percent of the collision rate. The results recently appeared in the literature. An analogous study was made on aluminum etching. While TiF was the etching product for titanium, $AlCl_3$ appears to leave the metal surface when plasma etched with chlorine containing compounds. The work is being prepared for publication.

The measurement of atoms was also applied to the production of metal films including both copper and tungsten. In both cases, metal atoms are made in the gas phase by reaction of H-atoms with metal precursors. Although the work requires further study for complete characterization of the deposited metal, the resultant films appear to be fine grained, adherent, and have good electrical properties. Reports of the work have been accepted for publication.

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OFFICE OF NAVAL RESEARCH

FINAL REPORT

for

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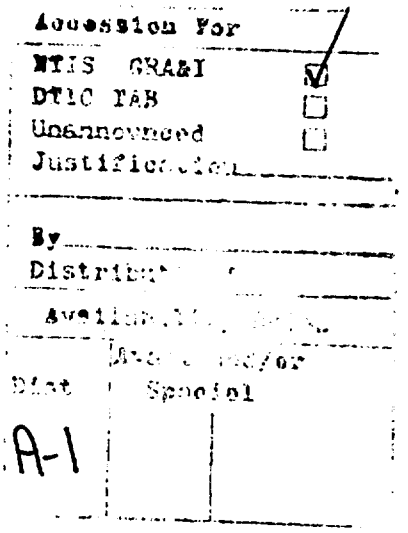

Entitled:

A Program in The Chemistry of Electronic Materials

(Prof. L. V. Interrante, Co-principal Investigator)

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Brief description of project:

The project was initiated with the intent to measure atoms in a dry etching plasma in order to obtain an insight into the mechanisms occurring. Atom measurements, both qualitative and quantitative, were made relatively easily, especially compared to those measurements needed for diatomic and triatomic radical species which are likely to be found under plasma conditions.

A series of probable reactions were developed to explain and model the process of etching of both titanium and aluminum metals. These provided the basis for a mechanism for the etching of each metal. Using steady-state assumptions, expressions for intermediate species were derived. Results of laboratory atom measurements were then compared with those expected from the mechanism proposed, and the model was then modified until a fit was obtained with the actual experimental results found.

Concentration measurements were made for both titanium and aluminum atoms while etching these metals, and relative atom measurements on the etching atom species of fluorine and chlorine respectively. The models have been developed, the probable mechanisms found, and the experimental data fitted to the equations derived for atom concentrations and various rate coefficients determined. The results on titanium have been published. A second publication on titanium is in preparation and also one on the work on aluminum.

As an outgrowth of the work on the study of atoms in etching, a study of the deposition of metal films was begun. Low temperature deposition of metals was accomplished with the focus of these efforts being on tungsten and copper, two important metals for the manufacture of integrated circuits. Preliminary measurements of the absolute gas phase concentrations of atom species of both tungsten and copper have been made using H-atoms as the active reactive species with the metal compound precursors. The metal deposits have been relatively free of impurities, adherent to most surfaces, and exhibit good electrical conductivity. Using a similar approach, preliminary work was performed on the production of metal oxide films which were found to be exceptionally conformal in nature.

Publications under this contract include:

1. "A Diagnostic Approach to Plasma Etching Kinetics: Determination of Atom Concentrations," by Reeves, Rutten, Ramaswami, Roessle, and Halstead; J. Electrochem. Soc. 137, 3517 (1990)

2. "A Spectroscopic Study of Vapor Phase Titanium Atoms," Ramaswami, Reeves, and Halstead; to be submitted to J. Quant. Spec. and Rad. Transfer

3. "An Investigation of the Kinetics of Aluminum Plasma Etching," Roessle, Reeves, and Halstead; to be submitted to J. Electrochem. Soc.

4. "Tungsten Film Deposition by Hydrogen Atom Reaction with WF_6," Lee, Reeves, and Halstead; accepted by J. Vac. Sci. Technol (to appear in May/June 1991 issue)

5. "Copper Film Deposition by Hydrogen Atom Reactions with Copper Compounds," Li and Reeves; accepted by J. Matls. Res. Soc.

Contributing to the work were:

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